

(19) Japanese Patent Office (JP)

(12) PATENT JOURNAL
(A)(11) Kokai Patent Application
No. 2002-356543

(43) Publication Date: December 13, 2002

(51) Int. Cl. ⁷ :	Identification Code	JPO File No.	FI	Theme Code (reference)
C 0 8 G 63/06 63/78	Z B P		C 0 8 G 63/06 63/78	Z B P 4 F 0 7 1 4 J 0 0 2
C 0 8 J 5/00	C F D		C 0 8 J 5/00	C F D 4 J 0 2 9
C 0 8 L 67/04			C 0 8 L 67/04	
Examination Request: Not requested		No. of Claims: 10 (Total of 13 pages; OL)		
(21) Application No.:	2002-69884(P2002-69884)		(71) Applicant:	000003159 Toray Industries, Inc. 2-2-1 Muro-cho, Nihonbashi, Chuo-ku, Tokyo-to
(22) Application Date:	March 14, 2002		(72) Inventor:	Sadaki Kumazawa Nagoya Business Field [Center], Toray Industries, Inc. 9-1 Oe-cho, Minato-ku, Nagoya-shi, Aichi-ken
(31) Priority Claim No.:	2001-95162		(72) Inventor:	Hirokazu Ome Nagoya Business Field, Toray Industries, Inc. 9-1 Oe-cho, Minato-ku, Nagoya-shi, Aichi-ken
(32) Priority Date	March 29, 2001		(72) Inventor:	Jiro Kumaki Nagoya Business Field, Toray Industries, Inc. 9-1 Oe-cho, Minato-ku, Nagoya-shi, Aichi-ken
(33) Priority Claim Country	Japan (JP)			
F term (reference):	4F071 AA43 AA75 AF45 AH01 AH03 AH07 AH11 AH12 BC01 BC07 4J002 BP00W CF18W CF18X CF19W FA04 FD01 FD03 FD05 FD06 FD09 FD13 FD16 FD17 GA00 GB00 GK00 GL01 GL00 GN00 GQ00 4J029 AA01 AA02 AB04 AC03 AD01 AE02 AE06 AE18 BA03 BA04 BA05 BF18 BF25 EA02 EH01 JC041 KB05 KE05			
(54) POLYLACTIC ACID BLOCK COPOLYMER, ITS MANUFACTURING METHOD, MOLDED PRODUCT, AND POLYLACTIC ACID COMPOSITION				
(57) Abstract				
Purpose: To provide a polylactic acid block copolymer for forming a polylactic acid stereocomplex with a high melting point, its manufacturing method, a molded product, and a polylactic acid composition.				
Solution means: A polylactic acid block copolymer characterized by being composed of a segment consisting of an L-lactic acid unit and a segment consisting of a D-lactic acid unit, its manufacturing method, a molded product, and a polylactic acid composition.				

[There are no amendments to this patent.]

CLAIMS

1. A polylactic acid block copolymer, characterized by being composed of a segment consisting of an L-lactic acid unit and a segment consisting of a D-lactic acid unit.
2. The polylactic acid block copolymer of Claim 1, characterized by the fact that the weight-average molecular weight of the above-mentioned polylactic acid block copolymer is 100,000 or more.
3. The polylactic acid block copolymer of Claims 1 and 2, characterized by the fact that the number of segments per molecule is 3 or more.
4. The polylactic acid block copolymer of any of Claims 1-3, characterized by the fact that at least part of each segment is coupled by a polyfunctional compound selected from a polyvalent carboxylic anhydride, polyvalent carboxylic halide, polyvalent carboxylic acid, polyvalent isocyanate, polyvalent amine, polyhydric alcohol, and polyvalent epoxy compound via a covalent bond.
5. A method for manufacturing the polylactic acid block copolymer of any of Claims 1-3, characterized by being manufactured by the following processes (1) and (2), the following processes (1)-(3), or the following processes (1)-(4):
 - (1) a first process that manufactures a polymer (I) consisting of an L-lactic acid or D-lactic acid unit, using a compound containing two or more hydroxyl groups or amino groups in the molecule as a polymerization initiator;
 - (2) a second process that manufactures a polymer (II) in which a segment having an antipode section consisting of a monomer unit of polymer (I) as a monomer unit is coupled with polymer (I);
 - (3) a third process that manufactures a polymer in which a segment having an antipode of a monomer unit of the segment coupled in the previous process as a monomer unit is coupled with the polymer obtained in the above-mentioned process;
 - (4) a fourth process that repeats process (3).
6. A method for manufacturing the polylactic acid block copolymer of any of Claims 1-4, characterized by being manufactured by (1) a process that manufactures a polymer (III) consisting of an L-lactic acid or D-lactic acid unit; (2) a process that manufactures a polymer (IV) in which a segment having an antipode section consisting of a monomer unit of polymer (III) as a monomer unit is coupled with polymer (III); and (3) a process that manufactures a polymer (V) by reacting polymer (IV) and a polyfunctional compound.
7. The method for manufacturing the polylactic acid block copolymer of Claim 5 or 6, characterized by the fact that the segment length satisfies $Y < X/2$, where the weight-average molecular weight of the polylactic acid block copolymer is X and the maximum weight-average molecular weight of one segment unit is Y.

8. A molded product, characterized by being constituted by molding the polylactic acid block copolymer of any of Claims 1-4.
9. A polylactic acid composition, characterized by being composed of (a) the polylactic acid block copolymer of any of Claims 1-4, (b) a poly-L-lactic acid, and (c) a poly-D-lactic acid.
10. A molded product, characterized by being constituted by molding the polylactic acid composition of Claim 9.

DETAILED EXPLANATION OF THE INVENTION

[0001]

Technical field of the invention

The present invention pertains to a polylactic acid block copolymer, its manufacturing method, a molded product, and a polylactic acid composition.

[0002]

Prior art

Recently, biodegradable polymers that are decomposed under a natural environment [in nature] by the action of microbes existing in soil and water have been studied in terms of environmental preservation, and various biodegradable polymers have been developed. Among them, as biodegradable polymers that can be melt-molded, for example, an aliphatic polyester composed of an aliphatic dicarboxylic acid component such as polyhydroxy butylate, polycaprolactone, succinic acid, and adipic acid, and a glycol component such as ethylene glycol and butanediol, polylactic acid, etc., are known.

[0003] Polylactic acid is relatively inexpensive, has heat resistance and a melting point of about 170°C, and is expected to be used as a biodegradable polymer that can be melt-molded. Also, since lactic acid as a monomer is inexpensively manufactured by a fermentation method using microbes and because the polylactic acid can be produced at lower cost, its utilization as a common polymer as well as a biodegradable monomer has been reviewed.

[0004] Furthermore, it is known that a polylactic acid stereocomplex is obtained by mixing a poly-L-lactic acid (hereinafter, called PLLA) and a poly-D-lactic acid (hereinafter, called PDLA) and is described in Japanese Kokai Patent Application Nos. Sho 61[1986]-36321 and Sho 63[1988]-241024, Macromolecules, 24, 5651 (1991), Japanese Kokai Patent Application No. 2000-17163, etc. It is known that the polylactic acid stereocomplex exhibits a high melting point and a high crystallinity and gives fibers, films, and useful molded products as resin molded products.

[0005] Also, in Japanese Kokai Patent Application No. Hei 9[1997]-40761, a polylactic acid block copolymer constituted by coupling a crystalline segment composed of PLLA or PDLA and an amorphous segment mainly composed of L-lactic acid and D-lactic acid is described.

[0006] Also, in Macromolecules, 24, 5651 (1991), it is described that the polylactic acid stereocomplex is difficult to be obtained from a combination of polylactic acids in which the molecular weights of PLLA and PDAL are high, especially a high molecular weight of 100,000 or more.

[0007]

Problems to be solved by the invention

However, in obtaining the polylactic acid stereocomplex by the methods of Japanese Kokai Patent Application Nos. Sho 61[1986]-36321 and Sho 63[1988]-241024, Macromolecules, 24, 5651 (1991), Japanese Kokai Patent Application No. 2000-17163, etc., it is necessary to prepare it by mixing PLLA and PDLA in a solution state or molten state.

[0008] When they were mixed in a solution state, it was necessary to add a solvent after mixing, and the manufacturing processes were complicated, so that the cost was raised.

[0009] Also, when they were mixed in a molten state, it was necessary to heat the polylactic acid stereocomplex at a sufficient melting temperature; the decomposition reaction of polylactic acid was simultaneously generated at that temperature, so the properties were lowered when it was used as a molded product.

[0010] Also, in order to achieve practical strength as a molded product, it was preferable to use a polylactic acid with a high molecular weight; however, in order to obtain a polylactic acid stereocomplex from a combination of polylactic acids with a high molecular weight, when these were mixed in a solution state, it was necessary to hold [leave undisturbed] the mixed solution for a long time, and when they were mixed in a molten state, a long kneading time was required. Thus, there was a problem in each of them in terms of productivity.

[0011] The method of Japanese Kokai Patent Application No. Hei 9[1997]-40761 was a method for improving the hardness and brittleness of the polylactic acid, but the melting point of the polylactic acid block copolymer obtained showed only a value lower than that of the PLLA or PDLA homopolymer, and the polylactic acid stereocomplex was not formed.

[0012] The present invention has been achieved as a result of a review of the problems in the above-mentioned prior art, and its objective is to provide a polylactic acid block copolymer for forming a polylactic acid stereocomplex with a high melting point, its manufacturing method, a molded product, and a polylactic acid composition.

[0013]

Means to solve the problems

These inventors reviewed the above problems in earnest to achieve the above-mentioned objective; as a result, it was discovered that a polylactic acid block copolymer characterized by being composed of a segment consisting of an L-lactic acid unit and a segment consisting of a D-lactic acid unit formed a polylactic acid stereocomplex with a high melting point.

The present invention was thus completed. In other words, the present invention provides the following.

(i) A polylactic acid block copolymer characterized by being composed of a segment consisting of an L-lactic acid unit and a segment consisting of a D-lactic acid unit.

(ii) The polylactic acid block copolymer described in (i), characterized by the fact that the weight-average molecular weight of the above-mentioned polylactic acid block copolymer is 100,000 or more.

(iii) The polylactic acid block copolymer described in (i) and (ii), characterized by the fact that the number of segments per molecule is 3 or more.

(iv) The polylactic acid block copolymer described in any of (i)-(iii), characterized by the fact that at least part of each segment is coupled by a polyfunctional compound selected from a polyvalent carboxylic anhydride, polyvalent carboxylic halide, polyvalent carboxylic acid, polyvalent isocyanate, polyvalent amine, polyhydric alcohol, and polyvalent epoxy compound via a covalent bond.

(v) A method for manufacturing the polylactic acid block copolymer described in any of (i)-(iii), characterized by being manufactured by the following processes (1) and (2), the following processes (1)-(3), or the following processes (1)-(4).

(1) A first process that manufactures a polymer (I) consisting of an L-lactic acid or D-lactic acid unit, using a compound containing two or more hydroxyl groups or amino groups in the molecule as a polymerization initiator.

(2) A second process that manufactures a polymer (II) in which a segment having an antipode section consisting of a monomer unit of the polymer (I) as a monomer unit is coupled with the polymer (I).

(3) A third process that manufactures a polymer in which a segment having an antipode section consisting of a monomer unit of the segment coupled in the previous process as a monomer unit is coupled with the polymer obtained in the above-mentioned process.

(4) A fourth process that repeats process (3).

(vi) A method for manufacturing the polylactic acid block copolymer described in any of (i)-(iv), characterized by being manufactured by (1) a process that manufactures a polymer (III) consisting of an L-lactic acid or D-lactic acid unit; (2) a process that manufactures a polymer (IV) in which a segment having an antipode section consisting of a monomer unit of polymer (III) as a monomer unit is coupled with polymer (III); and (3) a process that manufactures a polymer (V) by reacting polymer (IV) and a polyfunctional compound.

(vii) The method for manufacturing the polylactic acid block copolymer described in (v) or (vi), characterized by the fact that the segment length satisfies $Y < X/2$, where the weight-

average molecular weight of the polylactic acid block copolymer is X and the maximum weight-average molecular weight of one segment unit is Y.

(viii) A molded product characterized by being constituted by molding the polylactic acid block copolymer described in any of (i)-(iv).

(ix) A polylactic acid composition characterized by being composed of (a) the polylactic acid block copolymer described in any of (i)-(iv), (b) a poly-L-lactic acid, and (c) a poly-D-lactic acid.

(x) A molded product characterized by being constituted by molding the polylactic acid composition described in (ix).

[0014]

Embodiments of the invention

Next, the present invention is explained in detail. The polylactic acid block copolymer of the present invention is a polylactic acid block copolymer composed of a segment consisting of an L-lactic acid unit and a segment consisting of a D-lactic acid unit.

[0015] Here, the segment consisting of an L-lactic acid unit is a polymer mainly composed of L-lactic acid, and the L-lactic acid unit is contained at preferably 90 mol%, more preferably 95 mol% or more.

[0016] Also, the segment consisting of a D-lactic acid unit is a polymer mainly composed of D-lactic acid, and the D-lactic acid unit is contained at preferably 90 mol% or more, more preferably 95 mol% or more.

[0017] In the present invention, the segment consisting of an L-lactic acid or D-lactic acid unit may also include other constitutional units in a range wherein the performance of the polylactic acid block copolymer being obtained is not damaged. As constitutional components other than the L-lactic acid or D-lactic acid unit, a polyvalent carboxylic acid, polyhydric alcohol, hydroxycarboxylic acid, lactone, etc., can be mentioned; specifically, polyvalent carboxylic acids or their derivatives such as succinic acid, adipic acid, sebacic acid, fumaric acid, terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, 5-sodium sulfoisophthalic acid, and 5-tetrabutyl phosphonium sulfoisophthalic acid; polyhydric alcohols or their derivatives such as ethylene glycol, propylene glycol, butanediol, hexanediol, octanediol, neopentyl glycol, glycerin, and trimethylolpropane; aromatic polyhydric alcohols in which ethylene oxide is addition-reacted with bisphenol, diethylene glycol, triethylene glycol, polyethylene glycol, and polypropylene glycol; hydroxycarboxylates such as glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 4-hydroxyvaleric acid, and 6-hydroxycaproic acid; lactones such as glycolides, ϵ -caprolactone glycolide, ϵ -caprolactone, β -propiolactone, δ -butyrolactone, β - or γ -butyrolactone, pivalolactone, and δ -valerolactone, etc., can be mentioned.

[0018] In the present invention, the weight-average molecular weight of the polylactic acid block copolymer is not particularly limited, but 100,000 or more is preferable in terms of mechanical properties. In particular, 100,000-1,200,000 is preferable in terms of moldability and mechanical properties. Also, the weight-average molecular weight is a weight-average molecular weight value converted into [that of] a standard polymethyl methacrylate* measured by gel permeation chromatography (GPC) using hexafluoroisopropanol as a solvent.

[0019] Furthermore, in the present invention, it is preferable for the total number of segments consisting of the L-lactic acid unit included per molecule of the polylactic acid block copolymer and the segment consisting of the D-lactic acid unit to be 3 or more since a polylactic acid block copolymer that easily forms a polylactic acid stereocomplex with a high melting point can be obtained.

[0020] At least part of each segment is preferably coupled with a polyfunctional compound selected from a polyvalent carboxylic anhydride, polyvalent carboxylic halide, polyvalent carboxylic acid, polyvalent isocyanate, polyvalent amine, polyhydric alcohol, and polyvalent epoxy compound via a covalent bond.

[0021] Although the polyfunctional compound is not particularly limited, one can mention a polyvalent carboxylic anhydride, polyvalent carboxylic halide, polyvalent carboxylic acid, polyvalent isocyanate, polyvalent amine, polyhydric alcohol, polyvalent epoxy compound, etc. Specifically, a polyvalent carboxylic anhydride such as 1,2-cyclohexanedicarboxylic anhydride, phthalic anhydride, trimellitic anhydride, 1,8-naphthalenedicarboxylic anhydride, and pyromellitic anhydride, a polyvalent carboxylic halide such as isophthalic chloride, terephthalic chloride, and 2,6-naphthalenedicarboxylic chloride, a polyvalent carboxylic acid such as succinic acid, adipic acid, sebacic acid, fumaric acid, terephthalic acid, isophthalic acid, and 2,6-naphthalenedicarboxylic acid, a polyvalent isocyanate such as hexamethylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and toluene-2,4-diisocyanate, a polyvalent amine such as ethylenediamine, hexanediamine, and diethylenetriamine, a polyhydric alcohol such as ethylene glycol, propylene glycol, butanediol, hexanediol, glycerin, trimethylolpropane, and pentaerythritol, a polyvalent epoxy compound such as diglycidyl ester terephthalate, diglycidyl ester naphthalenedicarboxylate, triglycidyl ester trimellitate, tetraglycidyl ester pyromellitate, ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, cyclohexanedimethanol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, trimethylolpropane triglycidyl ether, and pentaerythritol polyglycidyl ether, etc., can be mentioned. A polycarboxylic anhydride, polyvalent isocyanate, polyvalent alcohol, and

* [Apparently meaning that polymethyl methacrylate is used as the standard to which the molecular weight is compared.]

polyvalent epoxy compound are preferable; in particular, a polyvalent isocyanate and polyvalent epoxy compound are more preferable.

[0022] The melting point of the polylactic acid block copolymer can be improved by coupling each segment with the polyfunctional compound via a covalent bond.

[0023] In the present invention, the total weight ratio of each of the segments consisting of the L-lactic acid unit and the segment consisting of the D-lactic acid unit is preferably 90:10-10:90, more preferably 75:25-25:75, and most preferably 60:40-40:60. If the weight ratio of the segment consisting of the L-lactic acid unit is respectively less than 10 weight [sic] and more than 90 weight [sic], the rise of the melting point of the polylactic acid block copolymer obtained is decreased, so that the polylactic acid stereocomplex is difficult to be formed.

[0024] Next, the method for manufacturing the polylactic acid block copolymer of the present invention is described. In the present invention, although the method for manufacturing the polylactic acid block copolymer is not particularly limited, it is preferably manufactured by the following processes (1) and (2), the following processes (1)-(3), or the following processes (1)-(4).

(1) A first process that manufactures a polymer (I) consisting of an L-lactic acid or D-lactic acid unit, using a compound containing two or more hydroxyl groups or amino groups in the molecule as a polymerization initiator.

(2) A second process that manufactures a polymer (II) in which a segment having an antipode section consisting of a monomer unit of the polymer (I) as a monomer unit is coupled with the polymer (I).

(3) A third process that manufactures a polymer in which a segment having an antipode of a monomer unit of the segment coupled in the previous process as a monomer unit is coupled with the polymer obtained in the above-mentioned process.

(4) A fourth process that repeats process (3).

[0025] First, first process (1) that manufactures the polymer (I) consisting of an L-lactic acid or D-lactic acid unit, using a compound containing two or more hydroxyl groups or amino groups in the molecule as a polymerization initiator, is mentioned in detail. Here, as the compound containing two or more hydroxyl groups or amino groups being used as a polymerization initiator, polyhydric alcohols such as ethylene glycol, propylene glycol, butanediol, hexanediol, octanediol, neopentyl glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, glycerin, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol, poly(vinyl alcohol), poly(hydroxyethyl methacrylate), and poly(hydroxypropyl methacrylate); polyvalent amines such as ethylenediamine, propylenediamine, butanediamine, hexanediamine, diethylenetriamine, and melamine, etc., can be mentioned; among them, a polyhydric alcohol is more preferable.

[0026] The amount of said polymerization initiator being added is not particularly limited, but it is preferably 0.001-5 parts by weight, more preferably 0.01-3 parts by weight, with respect to the raw materials being used (L-lactic acid, D-lactic acid, L-lactide, D-lactide, etc.) at 100 parts by weight. If the amount of polymerization initiator is less than 0.001 part by weight, the molecular weight of the polymer (I) is too large, whereas if the amount is more than 5 parts by weight, the molecular weight of the polymer (I) is too small. Thus, in any case, the polylactic acid block copolymer that is finally obtained is difficult to form a polylactic acid stereocomplex.

[0027] The method for manufacturing polymer (I) consisting of an L-lactic acid or D-lactic acid unit is not particularly limited, and a general method for manufacturing a polylactic acid can be employed. Specifically, a two-stage lactide method that generates a L-lactide or D-lactide as a ring-shaped dimer using an L-lactic acid or D-lactic acid as a raw material, and is subjected to an open-ring polymerization, a one-stage direct polymerization method that directly dehydrates and condenses said raw material in a solvent, etc., are known, but any manufacturing method may also be employed.

[0028] Also, with the use of a catalyst in the polymerization reaction, the polymerization time can be shortened. As the catalyst, for example, metals such as tin, zinc, lead, titanium, bismuth, zirconium, germanium, antimony, and aluminum and their derivatives can be mentioned. As the derivatives, a metal alkoxide, carboxylate, carbonate, oxide, and halide are preferable. Specifically, tin oxide, tin octylate, zinc chloride, zinc acetate, lead oxide, lead carbonate, titanium chloride, alkoxy titanium, germanium oxide, zirconium oxide, etc., can be mentioned. Among them, a tin compound is preferable; in particular, tin octylate is more preferable.

[0029] The amount of catalyst being added is not particularly limited, but it is preferably 0.001-2 parts by weight, more preferably 0.001-1 part by weight with respect to the raw materials being used (L-lactic acid, D-lactic acid, L-lactide or D-lactide, etc.) at 100 parts by weight. If the amount of catalyst is less than 0.001 part by weight, the shortening effect of the polymerization time is lowered, and if the amount is more than 2 parts by weight, a segment having a sufficient molecular weight for forming a polylactic acid stereocomplex is difficult to obtain.

[0030] Next, the second process (2) that manufactures polymer (II) in which a segment having an antipode section consisting of a monomer unit of polymer (I) as a monomer unit is coupled with polymer (I) is mentioned in detail.

[0031] As the method for manufacturing polymer (II), it can be manufactured by polymerizing a monomer for forming a segment coupled with polymer (I) in the presence of polymer (I), using a general method for manufacturing a polylactic acid. Also, with the use of a catalyst, the polymerization time can be shortened. Also, in this method, polymer (I) acts as a polymerization initiator, and the polymerization is advanced.

[0032] As the amount of polymer (I) being charged, the mole ratio of said terminal group of said polymer (I) and the monomer is preferably 1:30-1:4000, more preferably 1:35-1:2000, and most preferably 1:35-1:1000. If the mole number of the monomer to the mole number of the terminal group of polymer (I) is too large or too small, the polylactic acid block copolymer that is finally obtained is difficult to form a polylactic acid stereocomplex.

[0033] Next, the third process for manufacturing a polymer in which a segment having an antipode of a monomer unit of the segment coupled in the previous process as a monomer unit is coupled with the polymer obtained in the above-mentioned process is mentioned in detail.

[0034] As the method for manufacturing a polymer in which a segment having an antipode section consisting of a monomer unit of the segment coupled in the previous process as a monomer unit is coupled with the polymer obtained in the above-mentioned process, a monomer for forming a segment being coupled with the polymer obtained in the previous process can be manufactured by polymerizing using a general method for manufacturing a polylactic acid. Also, with the use of the catalyst, the polymerization time can be shortened. Also, in this method, the polymer obtained in the previous process acts as a polymerization initiator, and the polymerization is advanced.

[0035] As the amount of polymer obtained in the previous process being charged, the mole ratio of the terminal group of the polymer obtained in the previous process and the monomer is preferably 1:30-1:4000, more preferably 1:35-1:2000, and most preferably 1:35-1:1000. If the mole number of the monomer to the mole number of the terminal group of the polymer obtained in the previous process is too large or too small, the polylactic acid block copolymer that is finally obtained is difficult to form a polylactic acid stereocomplex.

[0036] Next, the fourth process is a process that repeats the above-mentioned third process.

[0037] With the manufacture through the above-mentioned processes (1) and (2), the above-mentioned processes (1)-(3), or the above-mentioned processes (1)-(4), the polylactic acid block copolymer of the present invention can be easily manufactured.

[0038] As another method for manufacturing a polylactic acid block copolymer of the present invention, (i) a process that manufactures a poly-L-lactic acid consisting of an L-lactic acid unit, (ii) a process that manufactures a poly-D-lactic acid consisting of a D-lactic acid unit, and (iii) a process that reacts the poly-L-lactic acid, poly-D-lactic acid, and polyfunctional compound are preferably carried out in the order of (i), (ii), and (iii). However, in order to more reliably obtain the polylactic acid block copolymer of the present invention, it is more preferably manufactured by (1) a process that manufactures a polymer (III) consisting of an L-lactic acid or D-lactic acid unit, (2) a process that manufactures a polymer (IV) in which a segment having an antipode section consisting of a monomer unit of the polymer (III) as a monomer unit is coupled with polymer (III), and (3) a process that manufactures a polymer (V) by reacting polymer (IV) and a

polyfunctional compound. Here, in order to easily manufacture the polylactic acid block copolymer with a high molecular weight and to easily form a polylactic acid stereocomplex, process (3) is most preferable.

[0039] First, process (1) that manufactures the polymer (III) consisting of an L-lactic acid or D-lactic acid unit is described.

[0040] The method that manufactures polymer (III) consisting of an L-lactic acid or D-lactic acid unit is not particularly limited, and a general method for manufacturing a polylactic acid can be employed. Also, with the use of a catalyst, the polymerization time can be shortened.

[0041] Next, process (2) that manufactures polymer (IV) in which a segment having an antipode section consisting of a monomer unit of the polymer (III) as a monomer unit is coupled with polymer (III) is mentioned in detail.

[0042] As the method for manufacturing polymer (IV), a monomer for forming a segment being coupled with polymer (III) can be manufactured by polymerizing in the presence of polymer (III), using a general method for manufacturing a polylactic acid. Also, with the use of the catalyst, the polymerization time can be shortened. Also, in this method, polymer (III) acts as a polymerization initiator, and the polymerization is advanced.

[0043] As the amount of polymer (III) being charged, the mole ratio of the terminal group of polymer (III) and the monomer is preferably 1:30-1:4000, more preferably 1:35-1:2000, and most preferably 1:35-1:1000. If the mole number of the monomer to the mole number of the terminal group of polymer (III) is too large or too small, the polylactic acid block copolymer that is finally obtained is difficult to form a polylactic acid stereocomplex.

[0044] Next, process (3) that manufactures polymer (V) by reacting polymer (IV) and a polyfunctional compound is discussed in detail.

[0045] As the method for manufacturing polymer (V), it can be manufactured by mixing polymer (IV) and the polyfunctional compound.

[0046] As the amount of polymer (IV) and polyfunctional compound being mixed, the mole ratio of the polymer (IV) and the polyfunctional compound is preferably 1:1-100:1, more preferably 1:1-50:1, and most preferably 1:1-10:1. If the mole number of the polyfunctional compound to the mole number of the polymer (IV) is too large or too small, the usage effect of the polyfunctional compound is reduced, so that polymer (IV) and polymer (V) are difficult to be differentiated.

[0047] Although the method for mixing polymer (IV) and the polyfunctional compound is not particularly limited, for example, a method that melt-kneads polymer (IV) and the polyfunctional compound by an extruder after dry-blending, a method that mixes polymer (IV) and the polyfunctional compound in a solvent and removes the solvent, etc., can be mentioned.

[0048] Polymer (V) is a polylactic acid block copolymer in which an L-lactic acid segment and a D-lactic acid segment are regularly arranged in an alternating manner, so that the molecular weight can be effectively increased.

[0049] In this manufacturing method, when the polylactic acid block copolymer of the present invention is manufactured, at least one molecular terminal, preferably both terminals, of the polymer obtained in each process are hydroxyl groups.

[0050] For this purpose, in process (1), as a polymerization initiator, a compound containing a hydroxyl group or amino group in the molecule is preferably used; a compound containing two hydroxyl groups or amino groups in the molecule is more preferable since there are many reaction points and a polylactic acid block copolymer can be efficiently manufactured. As the compound containing the hydroxyl groups or amino groups in the molecule, a monoalcohol such as butanol, pentanol, benzyl alcohol, and phenethyl alcohol, a polyhydric alcohol such as ethylene glycol, propylene glycol, butanediol, hexanediol, octanediol, neopentyl glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, glycerin, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol, poly(vinyl alcohol), poly(hydroxyethyl methacrylate), and poly(hydroxypropyl methacrylate), a monoamine such as butylamine, amylamine, benzylamine, and phenethylamine, or a polyvalent amine such as ethylenediamine, propylenediamine, butanediamine, hexanediamine, diethylenetriamine, and melamine can be mentioned. Among them, polyhydric alcohols and polyvalent alcohols are preferable since the manufacturing processes can be simplified and the cost can be reduced; in particular, a polyhydric alcohol is more preferable.

[0051] The amount of polymerization initiator being added is not particularly limited, but it is preferably 0.01-5 parts by weight, more preferably 0.01-3 parts by weight, with respect to the raw materials being used (L-lactic acid, D-lactic acid, L-lactide, D-lactide, etc.) at 100 parts by weight. If the amount of polymerization initiator is less than 0.001 part by weight, the molecular weight of polymer (III) is too large, whereas if the amount is more than 5 parts by weight, the molecular weight of polymer (III) is too small. Thus, in any case, the polylactic acid block copolymer that is finally obtained is difficult to form a polylactic acid stereocomplex.

[0052] Also, as another method for manufacturing the polylactic acid block copolymer of the present invention, it can be manufactured via a method for polymerizing a lactide racemic body using a specific catalyst (aluminum alkoxide, etc.).

[0053] In manufacturing the polylactic acid block copolymer of the present invention, its manufacturing method may be any of the above-mentioned manufacturing methods, and each process may be a batch method or continuous method. Also, the reactors are not particularly limited, and a stirring tank reactor, mixer reactor, tower reactor, extruder reactor, etc., can be used. Also, these reactors can be used in combinations of two or more.

[0054] The reaction temperature of each process is not particularly limited, but the reaction temperature is preferably in a range of 100-250°C, more preferably in a range of 120-230°C.

Also, in case the reaction is carried out in a molten state, it is preferable to carry out the reaction at the melting point, or higher, of the polymer in order to melt the polymer; however, in terms of suppression of the decomposition reaction, the reaction is preferably carried out by lowering the temperature, if possible, to the degree that the reaction product is not solidified.

[0055] Also, in case the reaction is carried out in a molten state, a solvent in which the polymer and the monomer are dissolved is used. As the solvent, for example, chloroform, methylene chloride, acetonitrile, etc., can be used. In case it is necessary to remove the solvent after reacting, the method for removing the solvent is not particularly limited; a method that volatilizes the solvent at room temperature, a method that volatilizes the solvent at the boiling point, or higher, of the solvent under reduced pressure, etc., can be employed.

[0056] The reaction pressure in each process is not particularly limited, so reduced pressure, normal pressure, and [high] pressurization may be employed.

[0057] Also, in each process, the reaction system inside is preferably set to a dry state, if possible. Drying L-lactic acids, etc., as raw materials or reacting in a dehumidified nitrogen atmosphere is effective for increasing the molecular weight of the polylactic acid block copolymer obtained.

[0058] In each process, the purification is preferably carried out so that no unreacted monomer remains. The purifying method is not particularly limited, and a method that dissolves the polymer in a solvent such as chloroform in which the polylactic acid is dissolved, and that precipitates the polylactic acid by the use of a solvent such as methanol in which polylactic acid is not dissolved, can be employed.

[0059] Next, it is preferable for the segment length to satisfy $Y < X/2$, where the weight-average molecular weight of the polylactic acid block copolymer of the present invention is X and the maximum weight-average molecular weight of one segment unit is Y . If the maximum weight-average molecular weight Y of one segment unit of the polylactic acid block copolymer is $Y \geq X/2$, the rise in the melting point of the polylactic acid block copolymer obtained is decreased, so that the polylactic acid stereocomplex is difficult to be formed. Also, the weight-average molecular weight of the above-mentioned one segment unit indicates the weight-average molecular weight of the segment formed in each process.

[0060] Also, the minimum weight-average molecular weight of one segment unit of the polylactic acid block copolymer is more preferably 5,000 or more. If the minimum weight-average molecular weight of one segment of the polylactic acid block copolymer is less than 5,000, the rise in the melting point of the polylactic acid block copolymer obtained is decreased, so that the polylactic acid stereocomplex is difficult to be formed.

[0061] Next, the polylactic acid composition of the present invention is explained. The polylactic acid composition of the present invention is a polylactic acid composition composed of (a) the above-mentioned polylactic acid block copolymer, (b) poly-L-lactic acid, and (c) poly-D-lactic acid.

[0062] In the present invention, as the method for manufacturing the poly-L-lactic acid (b) and the poly-D-lactic acid (c), a general method for manufacturing a polylactic acid such as the lactide method and direct polymerization method can be employed.

[0063] Also, in the poly-L-lactic acid (b) or poly-D-lactic acid (c), a small amount of component units other than the L-lactic acid (or D-lactic acid) unit may also be copolymerized to the degree that the purpose of the present invention is not damaged. As other components units, for example, a polyvalent carboxylic acid, polyhydric alcohol, hydroxycarboxylic acid, lactone, D-lactic acid (or L-lactic acid), D-lactide (or L-lactide), etc., can be mentioned.

[0064] (b) The weight-average molecular weight of the poly-L-lactic acid (b) and the poly-D-lactic acid (c) is not particularly limited, however, 100,000 or more is preferable to render a practical strength when this composition is used as a molded product.

[0065] The amount of polylactic acid block copolymer (a) being mixed is not particularly limited; however, the amount is preferably 1-200 parts by weight, especially preferably 10-100 parts by weight to the total amount of poly-L-lactic acid (b) and poly-D-lactic acid (c) at 100 parts by weight.

[0066] The mixture weight ratio of the poly-L-lactic acid (b) and the poly-D-lactic acid (c) is preferably 90:10-10:90, more preferably 75:25-25:75, and especially preferably 60:40-40:60.

[0067] The method for manufacturing the polylactic acid composition of the present invention is not particularly limited; however, for example, there is a method that dry-blends polylactic acid block copolymer (a), poly-L-lactic acid (b), and (c) poly-D-lactic acid, and melt-kneads it by the use of an extruder. The temperature at the time of the melt-kneading is preferably 160-250°C, more preferably 180-230°C.

[0068] Also, as another method for manufacturing the polylactic acid composition of the present invention, there is a method that mixes polylactic acid block copolymer (a), poly-L-lactic acid (b), and poly-D-lactic acid (c) in a solvent and obtains the polylactic acid composition by removing the solvent. As the solvent, for example, a solvent in which all the polymers such as chloroform are dissolved is used. The temperature at the time of mixing is not particularly limited as long as it is in a temperature range in which all the polymers are dissolved and the solvent is not volatilized. The method for removing the solvent is not particularly limited; for example, a method that volatilizes the solvent at room temperature, a method that volatilizes the solvent at the boiling point, or higher, of the solvent under reduced pressure, etc., can be employed.

[0069] In the polylactic acid block copolymer or polylactic acid composition of the present invention, ordinary additives, for example, one, two, or more types of filler (glass fibers, carbon fibers, metal fiber, natural fibers, organic fibers, glass flakes, glass beads, ceramic fibers, ceramic beads, asbestos, wollastonite, talc, clay, mica, sericite, zeolite, bentonite, montmorillonite, synthetic mica, dolomite, kaolin, fine powder silicic acid, feldspar powder, potassium titanate, Silas balloon, calcium carbonate, magnesium carbonate, barium sulfate, calcium oxide, aluminum oxide, titanium oxide, aluminum silicate, silicon oxide, gypsum, novaculite, dosonite, terra abla, etc.), ultraviolet absorbent (resorcinol, salicylate, benzotriazole, benzophenone, etc.), thermal stabilizer (hindered phenol, hydroquinone, phosphates, and their substituents), lubricant, mold release agent (montan acid and its salt, its ester, its hemi-ester, stearyl alcohol, stearamide, polyethylene wax, etc.), colorant containing dyes (nigrosine, etc.) and pigments (cadmium sulfide, phthalocyanine, etc.), anticoloring agent (phosphite, hypophosphite, etc.), flame retardant (red phosphorus, phosphoric ester, polystyrene bromide, bromated polyphenylene ether, brominated polycarbonate, magnesium hydroxide, melamine, cyanuric acid or its salt, etc.), electroconductive agent or colorant (carbon black, etc.), sliding enhancer (graphite, fluororesin, etc.), crystal nucleating agent (talc, organocarboxylic acid metal salt, etc.), antistatic agent, etc., can be added in a range in which the purpose of the present invention is not damaged.

[0070] In the polylactic acid block copolymer or polylactic acid composition of the present invention, at least one other thermoplastic resin (for example, polyethylene, polypropylene, acrylic resin, polyamide, polyphenylene sulfide resin, polysulfone, polyphenylene oxide, polyacetal, polyimide, polyether imide, etc.) or thermosetting resin (for example, phenol resin, melamine resin, polyester resin, silicone resin, epoxy resin, etc.), or soft thermoplastic resin (for example, ethylene/glycidyl methacrylate copolymer, polyester elastomer, polyamide elastomer, ethylene/propylene terpolymer, ethylene/butene-1 copolymer, etc.), etc., can be included.

[0071] The polylactic acid block copolymer or polylactic acid composition of the present invention can be broadly used as molded products. The molded products are films, sheets, fibers and fabrics, woven fabrics, injection-molded products, extruded products, vacuum air-pressure molded products, blow-molded products, and composites with other materials, and are useful as materials for agriculture, materials for horticulture, fishery materials, materials for civil works and construction, medical supplies, parts for automobiles, electric and electronic components, or other usages. In particular, it is useful as fibers such as clothes and various kinds of injection-molded products since the melting point and the crystallization rate are improved.

[0072]

APPLICATION EXAMPLES

Next, the present invention is explained in detail with application examples. Here, “part” in the application examples means “part by weight”.

[0073] The weight-average molecular weight, as mentioned above, is a weight-average molecular weight value converted into [that of] a standard polymethyl methacrylate measured by gel permeation chromatography (GPC). In the GPC measurement, a differential refractometer WATERS410 made by the WATERS Co., was employed as a detector, a MODEL 510 high-speed liquid chromatography was employed as a pump, and a Shodex GPC HFIP-806M and Shodex GPC HFIP-LG connected in series were used as a column. As the measurement conditions, the flow velocity was 0.5 mL/min, hexafluoroisopropanol was used as a solvent, and a solution with a sample concentration of 1 mg/mL was injected at 0.1 mL.

[0074] The molecular weight of the segment was calculated by the change in the weight-average molecular weight before and after reacting. Also, in case a polyfunctional compound was used as a polymerization initiator, the molecular weight of the segment of the polymer other than the homopolymer was set to a value in which the weight-average molecular weight difference before and after reacting was divided by the number of functional groups.

[0075] The weight ratio of L-lactic acid/D-lactic acid was calculated by the change in the weight-average molecular weight before and after reacting.

[0076] The melting point is a value measured by a differential scanning type calorimeter (DSC), and as the measurement conditions, 10 mg sample, nitrogen atmosphere, and a temperature-increase rate of 20°C/min were adopted. The formation of a polylactic acid stereocomplex was determined by the rise in the melting point. Also, the amount of polylactic acid stereocomplex being formed was determined by the level of the crystal melting enthalpy. In other words, if the melting point was raised and the crystal melting enthalpy was 10-20 J/g (this melting point peak is assumed as MP), the amount of polylactic acid stereocomplex being formed was increased. Furthermore, if the crystal melting enthalpy was 20 J/g or more (this melting peak is assumed as LP), it was decided that the amount of polylactic acid stereocomplex being formed was especially large.

[0077] On the other hand, even if the melting point was raised, if its peak had a crystal melting enthalpy of 5 J/g or less (this melting peak is assumed as SP), the amount of polylactic acid stereocomplex being formed was small, it was decided that a polylactic acid stereocomplex was not essentially formed.

[0078] Application Example 1

50 parts L-lactide and 0.08 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.2 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely

removed, so that a polymer (I) composed of an L-lactic acid unit [units], that is, a poly-L-lactic acid (P11), was obtained.

[0079] Next, 30 parts D-lactide and 15 parts of the P11 obtained were uniformly dissolved at 185°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 175°C, 0.1 part tin octylate was added to it and subjected to a polymerization reaction for 3 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer (II) in which segments consisting of a D-lactic acid unit were coupled with the P11, that is, a polylactic acid block copolymer (P12) with the segment number of 3, was obtained.

[0080] 15 parts L-lactide and 25 parts of the P12 obtained were uniformly dissolved at 190°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 180°C, 0.05 part tin octylate was added to it and subjected to a polymerization reaction for 4 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform, the solution was cast on a glass plate, held at room temperature for 12 h, and further dried at 80°C for 12 h under vacuum, so that a cast film of a polylactic acid block copolymer (P13) with the segment number of 5, in which segments consisting of an L-lactic acid unit were coupled with the P12, was obtained.

[0081] Application Example 2

100 parts L-lactide and 0.3 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.3 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer (I) composed of an L-lactic acid unit, that is, a poly-L-lactic acid (P21), was obtained.

[0082] 60 parts D-lactide and 30 parts of the P21 obtained were uniformly dissolved at 180°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 170°C, 0.2 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer (II) in which segments consisting of a D-lactic acid unit were coupled with the P21, that is, a polylactic acid block copolymer (P22) with the segment number of 3, was obtained.

[0083] 20 parts L-lactide and 30 parts of the P22 obtained were uniformly dissolved at 190°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 170°C,

0.08 part tin octylate was added and this was subjected to a polymerization reaction for 3 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polylactic acid block copolymer (P23) having 5 segments consisting of an L-lactic acid unit coupled with the P22 was obtained.

[0084] 10 parts L-lactide and 20 parts of the P23 obtained were uniformly dissolved at 190°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 185°C, 0.04 part tin octylate was added to it and subjected to a polymerization reaction for 3 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform; the solution was cast on a glass plate, held at room temperature for 12 h, and further dried at 80°C for 12 h under vacuum, so that a cast film of a polylactic acid block copolymer (P24) with the segment number of 7, in which segments consisting of an L-lactic acid unit were coupled with the P23, was obtained.

[0085] Application Example 3

50 parts L-lactide and 0.5 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.5 part tin octylate was added to it and subjected to a polymerization reaction for 1 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer (III) composed of an L-lactic acid unit, that is, a poly-L-lactic acid (P31) was obtained.

[0086] Next, 30 parts D-lactide and 25 parts of the P31 obtained were uniformly dissolved at 185°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 175°C, 0.3 part tin octylate was added to it and subjected to a polymerization reaction for 0.5 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer (IV) in which segments consisting of a D-lactic acid unit were coupled with the P31, that is, a polylactic acid block copolymer (P32) with the segment number of 3, was obtained.

[0087] 20 parts of the P32 obtained was uniformly dissolved at 180°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 175°C, 0.4 part 4,4'-diphenylmethane diisocyanate was added to it for 5 min and reacted for 1 h. The reaction product was dissolved in chloroform; the solution was cast on a glass plate, held at room temperature for 12 h, and further dried at 80°C for 12 h under vacuum, so that a polymer (V), that is, a cast film of a polylactic acid block copolymer (P33), was obtained.

[0088] Application Example 4

50 parts L-lactide and 0.5 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.5 part tin octylate was added to it and subjected to a polymerization reaction for 1 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer composed of an L-lactic acid unit, that is, a poly-L-lactic acid (P41), was obtained.

[0089] 50 parts D-lactide and 0.5 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 150°C, 0.5 part tin octylate was added to it and subjected to a polymerization reaction for 1 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer composed of a D-lactic acid unit, that is, a poly-D-lactic acid (P42), was obtained.

[0090] 10 parts of the P41 and 10 parts of the P42 obtained were uniformly dissolved at 180°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 175°C, 0.8 part 4,4'-diphenylmethane diisocyanate was added to it for 5 min and reacted for 1 h. The reaction product was dissolved in chloroform; the solution was cast on a glass plate, held at room temperature for 12 h, and further dried at 80°C for 12 h under vacuum, so that a cast film of a polylactic acid block copolymer (P43) was obtained.

[0091] Application Example 5

50 parts L-lactide and 0.06 part benzyl alcohol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.2 part tin octylate was added to it and subjected to a polymerization reaction for 3 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer composed of an L-lactic acid unit, that is, a poly-L-lactic acid (P51), was obtained.

[0092] 20 parts D-lactide and 20 parts of the P51 obtained were uniformly dissolved at 175°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 170°C, 0.1 part tin octylate was added and this was subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polylactic acid block copolymer (P52) having 2 segments consisting of a D-lactic acid unit coupled with the P51 was obtained.

[0093] Application Example 6

50 parts L-lactide and 0.02 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature set to 150°C, 0.05 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a polymer (I) composed of an L-lactic acid unit, that is, a poly-L-lactic acid (P61), was obtained.

[0094] 15 parts D-lactide and 30 parts of the P61 obtained were uniformly dissolved at 185°C under a nitrogen atmosphere in the reactor with a stirrer; after setting the temperature to 175°C, 0.08 part tin octylate was added to it and reacted for 1 h. The reaction product was dissolved in chloroform, and the solution was cast on a glass plate, held at room temperature for 12 h, and further dried at 80°C for 12 h under vacuum, so that a polymer (II) in which 3 segments composed of a D-lactic acid unit were coupled with the P61, that is, a cast film of a polylactic acid block copolymer (P62), was obtained.

[0095] Application Example 7

100 parts L-lactide and 0.04 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.05 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a poly-L-lactic acid (P71) composed of an L-lactic acid unit was obtained.

[0096] 100 parts D-lactide and 0.04 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.05 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a poly-D-lactic acid (P72) composed of a D-lactic acid unit was obtained.

[0097] 30 parts of the P71, 30 parts of the P72, and 30 parts of the P13 obtained in Application Example 1 were melt-kneaded (a residence time of 2 min) by a biaxial extruder, so that a polylactic acid (P73) pellet was obtained.

[0098] Comparative Example 1

50 parts L-lactide and 0.02 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.03 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the

polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a poly-L-lactic acid (P81) composed of an L-lactic acid unit was obtained.

[0099] 50 parts D-lactide and 0.02 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer, and after setting the temperature set to 150°C, 0.03 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a poly-D-lactic acid (P82) composed of a D-lactic acid unit was obtained.

[0100] 10 parts of the P81 and 10 parts of the P82 were respectively dissolved in chloroform and mixed for 10 min. The mixture was cast on a glass plate, held at room temperature for 12 h, and further dried at 80°C for 12 h under vacuum, so that a cast film of polylactic acid (P83) was obtained.

[0101] Comparative Example 2

50 parts L-lactide and 0.04 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.1 part tin octylate was added to it and subjected to a polymerization reaction for 1 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a poly-L-lactic acid (P91) composed of an L-lactic acid unit was obtained.

[0102] 50 parts D-lactide and 0.04 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.1 part tin octylate was added to it and subjected to a polymerization reaction for 1 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a poly-D-lactic acid (P92) composed of a D-lactic acid unit was obtained.

[0103] 10 parts of the P91 and 10 parts of the P92 were respectively dissolved in chloroform and mixed for 10 min. The mixture was cast on a glass plate, held at room temperature for 12 h, and further dried at 80°C for 12 h under vacuum, so that a cast film of polylactic acid (P93) was obtained.

[0104] Comparative Example 3

50 parts L-lactide and 0.02 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.05 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in

methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a poly-L-lactic acid (P101) composed of an L-lactic acid unit was obtained.

[0105] 50 parts D-lactide and 0.05 part ethylene glycol were uniformly dissolved at 120°C under a nitrogen atmosphere in a reactor with a stirrer; after setting the temperature to 150°C, 0.05 part tin octylate was added to it and subjected to a polymerization reaction for 2 h. After finishing the polymerization reaction, the reaction product was dissolved in chloroform and precipitated in methanol (an amount 10 times that of chloroform) while stirring; the monomer was completely removed, so that a poly-D-lactic acid (P102) composed of a D-lactic acid unit was obtained.

[0106] 30 parts of the P101 and 30 parts of the P102 were melt-kneaded (a residence time of 2 min) by a biaxial extruder, so that a pellet of polylactic acid (P103) was obtained.

[0107] For each polymer obtained, their GPC and DSC were measured; the results are shown in Table 1.

[0108]
(Table 1)

Table 1

	Polymer	Weight-average molecular weight. $\times 10^{-3}$	Molecular weight of segment		L-lactic acid/D-lactic acid weight ratio	Melting point		
			Minimum $\times 10^{-3}$	Maximum $\times 10^{-3}$		LP ^{*1} °C	MP ^{*2} °C	SP ^{*3} °C
Application Example 1	P11	33	33	33	100/0	188		
	P12	97	32	33	34/66			
	P13	153	28	33	58/42	221		
Application Example 2	P21	20	20	20	100/0	168		
	P22	58	18	20	36/64			
	P23	88	18	20	59/41			
	P24	125	18	20	41/59	219		
Application Example 3	P31	8	8	8	100/0	158		
	P32	12	3	8	67/33			
	P33	159	8	8	50/50	224		
Application Example 4	P41	8	8	8	100/0	158		
	P42	8	8	8	0/100	158		
	P43	158	—	—	50/50	223		174
Application Example 5	P51	85	85	85	100/0	175		
	P52	168	83	85	61/49	176	213	
Application Example 6	P61	140	140	140	100/0	175		
	P62	200	30	140	79/20	178	207	
Application Example 7	P71	154	154	154	100/0	178		
	P72	153	153	153	0/100	178		
	P73	155	153	153	54/46	218		176
Comparative Example 1	P81	150	150	150	100/0	175		
	P82	148	148	148	0/100	175		
	P83	148	—	—	50/50	178		
Comparative Example 2	P91	85	85	85	100/0	175		
	P92	84	84	84	0/100	175		
	P93	84	—	—	50/50	224		
Comparative Example 3	P101	140	140	140	100/0	175		
	P102	139	139	139	0/100	175		
	P103	115	—	—	50/50	173		214

*1: LP represents a melting point peak with a crystal melting enthalpy of 20 J/or or more in the polymer melting point peak.

*2: MP represents a melting point peak with a crystal melting enthalpy of 10-20 J/or or more in the polymer melting point peak.

*3: SP represents a melting point peak with a crystal melting enthalpy of 5 J/or or less in the polymer melting point peak.

[0109] As shown in Application Examples 1-6, the polylactic acid block copolymer of the present invention exhibited a MP or LP of 200°C or higher, and the melting point was raised. The copolymer easily formed a polylactic acid stereocomplex without mixing the poly-L-lactic acid and the poly-D-lactic acid. Also, as shown in Application Example 7, in the polylactic acid composition of the present invention, the melting point could be effectively raised, and the composition formed a polylactic acid stereocomplex.

[0110] On the other hand, as shown in Comparative Example 1, the combination of the poly-L-lactic acid and the poly-D-lactic acid had a high molecular weight of 100,000 or more, the rise in the melting point was not seen, and no polylactic acid stereocomplex was formed. As shown in Comparative Example 2, if the combination of the poly-L-lactic acid and the poly-D-lactic acid

had a low molecular weight of 100,000 or less, the melting point was raised, and a polylactic acid stereocomplex was formed. However, a complicated solution mixture was adopted in the process, and the weight-average molecular weight of the polymer obtained was 100,000 or less. Also, as shown in Comparative Example 3, in the melt-kneading method having a residence time of 2 min, the rise in the melting point was not seen (neither MP nor LP was seen; only SP was seen), and no polylactic acid stereocomplex was formed.

[0111] Furthermore, for P13 of Application Example 1, P24 of Application Example 24, P33 of Application Example 3, P83 of Comparative Example 1, P93 of Comparative Example 2, and P103 of Comparative Example 3, films with a thickness of 0.1 mm were prepared by pressing at 250°C for 5 min, and the amount of heat was measured using a differential scanning calorimeter (DSC). As the measurement conditions, 10 mg sample, nitrogen atmosphere, and the following temperature program (1st Run and 2nd Run) were adopted.

1st Run

The temperature was raised from 30°C to 250°C at a temperature-increase rate of 20°C/min, held at 250°C for 5 min, and dropped to 30°C at a temperature-drop rate of 20°C/min.

2nd Run

The temperature was held at 30°C for 1 min and raised to 250°C at a temperature-increase rate of 20°C/min.

[0112] The results of each melting point T_m in the 1st Run and 2nd Run and the temperature-drop crystallization peak (T_c) in the 1st Run are shown in Table 2. Also, the melting point T_m described in Table 2 is a peak in which the crystal melting enthalpy is 20 J/g or more.

[0113]

(Table 2)

Table 2

	Polymer		1st Run		2nd Run
	Name	T_m^{*1} °C	T_m^{*1} °C	T_c^{*2} °C	T_m^{*1} °C
Application Example 1	P13	221	218	112	217
Application Example 2	P24	218	215	115	215
Application Example 3	P33	224	220	118	219
Comparative Example 1	P83	176	176	n.m. ^{*3}	175
Comparative Example 2	P93	224	210	n.m. ^{*3}	188
Comparative Example 3	P103	173	173	n.m. ^{*3}	171

*1: A melting point peak in which the crystal melting enthalpy is 20 J/g or more

*2: Temperature drop crystallization peak

*3: Cannot be measured

[0114] As shown in Application Examples 1-3, in the polylactic acid block copolymer of the present invention, even if the thermal melting was repeated, the decrease in the melting point

was small, and the crystallization enthalpy at the time of the temperature drop was large. On the other hand, as shown in Comparative Examples 1-3, the melting point was largely lowered by the thermal melting in the combination of the poly-L-lactic acid and the poly-D-lactic acid, and the crystallization enthalpy at the time of the temperature drop was small. Therefore, according to the present invention, a polylactic acid block copolymer for forming a polylactic acid stereocomplex, which could maintain a high melting point even if the thermal melting was repeated and the crystallization rate was raised, could be obtained.

[0115]

EFFECTS OF THE INVENTION

According to the present invention, use is made of a polylactic acid block copolymer composed of a segment consisting of an L-lactic acid unit and a segment consisting of a D-lactic acid unit, so that a polylactic acid block copolymer for effectively forming a polylactic acid stereocomplex with a high melting point is obtained. Also, if the polylactic acid block copolymer of the present invention is provided, a high melting point can be maintained, regardless of the thermal fusion history, and a polylactic acid copolymer for forming a polylactic acid stereocomplex in which the crystallization rate was raised is obtained. Also, its manufacturing method and molded product can be provided. Also, according to the present invention, a polylactic acid composition that can form a polylactic acid stereocomplex from the combination of a high-molecular-weight polylactic acid and its molded product, can be provided.

Language Services Unit
Phoenix Translations
April 4, 2007